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Magnetic influence on thermoelectric properties of $CrO_{0.1}N_{0.9}$

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Abstract

Thermoelectric polycrystalline chromium oxynitride $CrO_{0.09(3)}N_{0.90(7)}$ (with cubic symmetry and space group *Fm-3m*) samples were successfully prepared by thermal ammonolysis of chromium oxide. This potential *n*-type thermoelectric material shows a temperature dependence of the Seebeck coefficient ($S = -48\ \mu V\ K^{-1}$ at 300 K) that is typical for degenerate semiconductors; the electrical resistivity ($\rho_{300} \sim 2.8\ m\Omega\ cm$), however, is highly influenced by the grain boundaries and low density (~60%) of the sample. The material exhibits a clear antiferromagnetic–paramagnetic transition simultaneously with an orthorhombic–cubic structural transition at $T_N = 262$ K. The magnetic transition affected the material's thermal conductivity, electrical resistivity, Seebeck coefficient, magnetic moment and specific heat. Heat capacity measurements at low temperatures revealed the predominance of the magnetic contribution due to spin waves.
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Keywords: Chromium oxynitride; Electrical properties; Thermal conductivity; Magnetic properties; Specific heat

1. Introduction

Conventional thermoelectric materials, such as tellurides, are limited for applications at elevated temperatures in air due to evaporation and corrosion processes. Thus, for the last few years alternative ceramic materials have been considered and developed for high-temperature thermoelectric applications [1–3]. Among them transition metal oxynitrides are a fascinating class of ceramic materials with interesting thermoelectric, magnetic and electronic properties [4]. They can be produced by thermal ammonolysis of oxide precursors [5].

Transition metal nitrides are chemical- and corrosion-resistant and possess good mechanical properties [6]. In addition, they exhibit relatively low electrical resistivities associated with large Seebeck coefficients (e.g. CrN: $S = -135\ \mu V\ K^{-1}$ at $T = 300$ K). Thus, CrN can be considered as a promising thermoelectric material [7]. 3*d* transition metal nitrides exist in different crystal lattice structures. Most of them (e.g. ScN, TiN, VN, CrN) have a rock-salt (RS) structure with a small lattice constant ($a < 4.25$ Å); others (i.e. MnN, FeN and CoN) crystallize in the zinc blende (ZB) structure with a larger lattice constant (4.2 Å $< a <$ 4.6 Å) [8–12]. The influence of the lattice constants and the cohesive energy on the magnetic properties of 3*d* transition metal nitrides was reported in Ref. [11]. Cohesive energy calculations confirm that early transition metal nitrides (ScN, TiN, VN, CrN) prefer a RS crystal structure, and the later metal nitrides (from MnN) a ZB structure. The influence of the lattice parameter on the magnetic moment is stronger in the RS than in the ZB crystal structure due to possible nanosized precipitates in the ZB phase inducing ferromagnetic (FM) ordering. 3*d* transition metal nitrides show interesting properties like antiferromagnetism, Pauli paramagnetism and superconductivity [13,8]. For example, thin films of solid solutions of $Cr_{1-x}Ti_xN$ have a large magnetoresistance [14]. In the range of $0.28 \leqslant x \leqslant 0.50$ these compounds are ferromagnetic, which results from the competition between

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antiferromagnetic (AFM) interactions of half-filled Cr t_{2g} orbitals and interactions governed by the Cr (Ti)–N–Cr (Ti) double-exchange mechanism. Using epitaxial thin films, it was shown that the orientations of the thin films influence the structural transformation and thereby the material properties regardless of the substrate material [15].

CrN is the only nitride that shows an antiferromagnetic–paramagnetic transition with a Neel temperature of $273\ \mathrm{K} < T_N < 286\ \mathrm{K}$, a magnetic moment of 2.4 μ_B and metallic behavior [16–18]. At the same time, CrN undergoes a structural transition from a low-temperature orthorhombic structure (with a small orthorhombic distortion below T_N) to a high-temperature cubic structure accompanied by a ~0.59% change in the unit cell volume [16,18]. Using the local spin density functional theory, the magnetic structure of CrN was described as (1 1 0) FM layers with alternating spins every two layers, so that the system is AFM overall. The magnetic behavior of CrN indicates the competition between the superexchange (AFM) and the double-exchange (FM) mechanism [19]. The magnetic and structural transitions are also revealed by a clear hysteresis of the electrical and thermal transport properties of CrN. Thus, a similar behavior is expected of $CrO_{0.09(3)}N_{0.90(7)}$.

The aim of this work is to study the thermoelectrical properties of $CrO_{0.09(3)}N_{0.90(7)}$, i.e. the Seebeck coefficient (S), the electrical resistivity (ρ) and the thermal conductivity (κ) with regard to a possible thermoelectric application. The influence of the magnetic properties on the heat capacity and the transport properties is explained by drawing an analogy to the Cr^{2+}/Cr^{3} mixed valence compounds $Cr_{1-x}Ti_xN$ and $Cr_{1-x}V_xN$.

2. Experimental

$Cr(NO_3)_3{\cdot}9H_2O$ was dissolved in deionized water and precipitated in a NH_3 (28–30% aq.) solution. The precipitate was washed twice with deionized water and dried at $T = 373$ K for 12 h and $T = 723$ K for 1 h to yield a single phase Cr_2O_3 as confirmed by X-ray powder diffraction (XRPD). The oxide was reacted with ammonia (PanGas, 99.98%, 200 ml min^{-1}) at $T = 1173$ K and $T = 1268$ K for 4 h and 2 h, respectively. The reactions were carried out in a rotation cavity quartz (SiO_2) reactor [20] with an internal diameter of 30 mm. The ceramic pellets were obtained by uniaxial pressing of the ammonolized powder at 10 bar followed by sintering at $T = 1268$ K for 2 h under ammonia. The sample was cooled down to room temperature under ammonia at a cooling rate of 10 K min^{-1}. The bulk sample had a density of ~60% of the theoretically achievable density.

Structure, phase composition and size-strain parameters of the starting and product powders were studied by X-ray powder diffraction (XRPD) using a Phillips X'Pert PRO MPD Θ–Θ System equipped with a linear detector X'Celerator. Crystallographic parameters were obtained from Rietveld refinement of the XRPD data collected in angular range of $25° < 2\Theta < 135°$ in 0.017° increments and a counting time of 250 s per step. The background was modeled by a sixth-degree polynomial function and the diffraction peak shape by a pseudo-Voigt profile. All the refinements were performed using FULLPROF [21].

Powder samples were dispersed in methanol, dropped on carbon-film coated copper grids and dried in air. Transmission electron microscopy (TEM) was performed using a Philips CM 30 microscope at 300 kV equipped with an EDX INCA detector from Oxford Instruments.

The O/N content of the sample was determined by hot gas extraction (HGE) using a LECO TC500 analyzer [22]. About 50 mg of the sample was placed in a tin container positioned in a double graphite crucible and heated up to $T = 3273$ K for carbothermal reduction. The nitrogen was measured as N_2 by a thermal conductivity cell and oxygen was measured as CO_2 in an IR cell. Silicon nitride and silicon oxide were used as calibration standards for nitrogen and oxygen, respectively.

The thermal stability was measured by thermogravimetric analysis/differential thermal analysis (TGA/DTA) using a Netzsch STA 409 CD thermobalance in the temperature range of $300\ \mathrm{K} < T < 1300\ \mathrm{K}$ with a heating rate of 10 K min^{-1} under a synthetic air atmosphere (20 vol.% O_2/He).

The Seebeck coefficient, thermal conductivity and electrical resistivity measurements were carried out using a self-built system [23] within the temperature range of $3\ \mathrm{K} < T < 300\ \mathrm{K}$. The four-point steady-state method with separated sensors and power contacts was applied. The principle and details of low-temperature measurements can be found in Ref. [23]. At high temperatures ($300\ \mathrm{K} < T < 850\ \mathrm{K}$) the Seebeck coefficient and the electrical resistivity were measured in air using the RZ2001i Ozawa Science, Japan measurement system.

The magnetic susceptibility was measured using a vibrating sample magnetometer (VSM) adaptor for the physical property measurement system (PPMS) from Quantum Design in the temperature range of $4\ \mathrm{K} < T < 400\ \mathrm{K}$. The measurements were performed applying a field of 0.1 T on zero field-cooled (ZFC) and on field-cooled (FC) samples. Magnetization curves were obtained at $T = 10$ K in the field range of $-5\ \mathrm{T} < H < 5\ \mathrm{T}$.

The high temperature heat capacity was studied at a heating rate of 20 K min^{-1} and a gas flow rate of 50 ml min^{-1}under a synthetic air atmosphere (20 vol.% O_2/He). A heat capacity puck for the PPMS was used in the temperature range of $2.3\ \mathrm{K} < T < 335\ \mathrm{K}$ and a Netzsch differential scanning calorimeter (DSC) 404 C Pegasus in the temperature range of $373\ \mathrm{K} < T < 700\ \mathrm{K}$.

3. Results

The chemical composition of the sample was determined to be $CrO_{0.09(3)}N_{0.90(7)}$. The oxygen content was estimated using EDX spectroscopy coupled with TEM. The exact concentration was measured by hot gas extraction resulting

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